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Reducing Flammability for Bakken Crude Oil for Train Transport - Phase IV

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**Reducing Flammability for Bakken Crude Oil for Train Transport
Final Report for 2021 – Phase IV**

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16. Abstract Crude oil shipping by rail is a critical component of our energy security and has grown steadily with the Bakken oil boom. However, existing rail infrastructure is in a state of disrepair which is evidenced by several recent, high-profile derailments of trains carrying crude oil resulting in large oil spills. This is an especially dangerous situation in the case of Bakken crude, which is of a light variety and contains significant amounts of easy to evaporate, easy to ignite, light ends, and usually the result is an intense fireball. Previous research done by Professor Albert Ratner's research group under MATC-DOT sponsorship has concluded that polymeric additives improve fire safety in diesel fuels and its blends by delaying ignition, promoting flame extinction, and suppressing splashing. There is a strong indication that the same will be true for crude oil as well. As of December 31, 2021, research efforts continued the work that would help accomplish the goals of a larger, five-year project to improve fire safety during transportation by adding long-chain polymers and carbon-based nanoadditives to crude oil before shipping. Surrogates for the Bakken crude were identified and tested for their ability to suspend polymers and nanoparticles that will serve as the fire limiting agents. Combustion characteristics were established for surrogate fuels with nanoadditives which is expanded with Bakken and Pennsylvania crudes containing various polymeric additives at various concentrations. Also, the stability/settling characteristics were investigated with different surrogate fuels. This work has resulted in several published manuscripts, and they are expected to help in the modeling of the combustion characteristics of crude oil and how to make crude oil transport safer.					
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List of Abbreviations and Nomenclature

API = American Petroleum Institute (Gravity)
EIA = Energy Information Administration
MCF = Motor Coach Fire
MUX = Multiplexer
PBD = Polybutadiene
PANI = Polyaniline
SEL = Select (Channel select)
VGO = Vacuum Gas Oil
FSR = Flame stand-off ratio
SEM = Scanning electron microscope
CD = Carbon Dot

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Abstract

Crude oil shipping by rail is a critical component of our energy security and has grown steadily with the Bakken oil boom. However, existing rail infrastructures is in a state of disrepair, with several recent high-profile derailments of trains carrying crude oil resulting in large oil spills. This is an especially dangerous situation in the case of Bakken crude, which is of a light variety and contains significant amounts of easy-to-evaporate and easy-to-ignite light ends, and usually the result is an intense fireball. Previous research done by Professor Albert Ratner's research group under MATC-DOT sponsorship has concluded that polymeric additives improve fire safety in diesel fuels and its blends by delaying ignition, promoting flame extinction, and suppressing splashing. There is a strong indication that the same will be true for crude oil as well. As of December 31, 2021, research efforts continued the work that would help accomplish the goals of a larger, five-year project to improve fire safety during transportation by adding long-chain polymers and carbon-based nanoadditives to crude oil before shipping. Surrogates for the Bakken crude were identified and tested for their ability to suspend polymers and nanoparticles that will serve as fire limiting agents. Combustion characteristics were established for surrogate fuels with nanoadditives, and expanded with Bakken and Pennsylvania crudes, containing various polymeric additives at various concentrations. Also, the stability/settling characteristics were investigated with different surrogate fuels. This work has resulted in several published manuscripts and is expected to help the community model the combustion characteristics of crude oil and how to modify them to make crude oil transport safer.

Chapter 1 Introduction

Several high-profile incidents in recent years involving oil train crashes and devastating oil fires [1] [2] [3] have raised concerns regarding the safety of oil transportation via rail. Rail transportation of crude oil is critical for the energy security of the United States: in February 2015, crude oil shipping by rail accounted for more than half of the East Coast refinery supply [4]. The latest annual data from the US Energy Information Administration (EIA) indicates that shipments out of the Midwest to other US regions via rail steadily increased from 2010 to 2015 [5]. This data directly correlates to the Bakken oil boom, which peaked in 2012. Transportation of Bakken oil via extant rail system is a major safety concern, since it is of a very light and sweet variety, with a typical API gravity of 42 [6].

There is consensus that the US rail infrastructure is in a state of neglect and will need significant overhaul to handle current and future freight congestion. This can be expected to result in long delays, which regrettably means that more crude oil freight car derailments must be planned for. The Motor Coach Fire (MCF) database identifies hot wheel wells as a common origin of fires [7]. Any derailment or crash typically leads to an oil spill in the region, with hot surfaces like wheel wells present in abundance on the site. Bakken oil, especially, contains significant amounts of light ends [6], characterized by high volatility and low ignition temperatures. In the event of a derailment and subsequent oil spill, they rapidly evaporate and catch fire.

One possible prevention method is to remove light ends from the crude before shipping it. This is already being done in Texas and California before shipping the crude (typically via pipeline). Another option is to flare them, which happens in offshore oil derricks or in remote oil fields. In North Dakota's case, the likelihood of having a light-end capturing system in operation

or the creation of a new pipeline to obviate the need for shipping by rail is very low.

Furthermore, flaring off light ends is tightly regulated by the EPA under the Clean Air Act, meaning this option is also very unlikely.

This report is for year four of a five-year investigation into a solution that can act as both a stopgap and a long-term measure to control derailment-related oil fires: polymeric additives and carbon-based nanoadditives that minimize the risk of fire initiation, slow down the combustion process, and enhance its extinction. Previous work done by this research group has concluded that adding long-chain polymers to diesel and its blends suppresses mist formation and splashing [8]. Additionally, studies have shown that this additive can suppress soot formation [9], a process known to result in the formation of highly flammable hydrogen gas. Moreover, adding long-chain polymers to diesel and Jet-A droplets [10] as well as their surrogate blends [13][14][15] retards their burning rate and increases ignition delay.

It is found that the addition of long-chain polymers and carbon-based nanoparticles to crude oil similarly results in less splattering, less mist generation, less soot formation, and increased ignition delay, all of which are contributing factors to better fire safety of crude during transportation. In addition, crude pipelines use polymers as drag reducing agents [11] [12], and logistical infrastructure to handle them is in place.

Work undertaken during year four focused heavily on quantification of crude oil combustion properties with polymeric additives [16], exploring the prospects of using a biocompatible nanoadditive with crude surrogate as a combustion behaviors modifier [19], and establishing combustion trends for different emulsified fuels based on the crude surrogate [17]. Combustion trends data were generated for Bakken and Pennsylvania crudes with a polybutadiene polymer. Also, the combustion characteristics of carbon dots with Jet-A were

explored. Carbon dots are a new class of noble biocompatible nanoadditives while Jet-A can be considered as a multicomponent surrogate for crudes. In addition, stability and combustion behaviors of different emulsified fuels based on Jet-A (base fuel), water and ethanol were investigated. These studies have resulted in two journal papers (one has been published and one is under review), three conference papers, and other manuscripts that are under development. This material will also aid in theoretical combustion modeling of complex multicomponent liquid fuels like crude oil, as well as generate interest in investigating more polymeric additives and carbon-based nanoadditives for liquid fuels.

Chapter 2 Major Activities and Results

2.1 Combustion data generation

The effect of polymeric additives (polybutadiene polymer) on ignition, combustion, and flame characteristics and soot deposits of crude oil (Bakken and Pennsylvania crudes) droplets were investigated experimentally. Combustion data was also generated for carbon dots as nanoadditive and Jet-A as base fuel. In addition, stability and combustion behaviors of different emulsified fuels based on Jet-A (base fuel), water, and ethanol were investigated. These experimental data provide a wider look into modeling the combustion behavior of crude oil and other liquid fuel. First, using the droplet combustion setup (Figure 2.1), combustion data was generated for the combustion characteristics of Bakken and Pennsylvania crudes with polybutadiene polymer. These data aid in further evaluation of potential combustion substitutes. This information is needed before any attempt is made to modify these crude oils' characteristics. Also, combustion data was generated for Jet-A with carbon dots. Combustion properties of nano-fuels were found to be significantly different and might need different control strategies to increase ignition delay and decrease combustion rates [13][20]. Polymer addition can decrease ignition delay and combustion rate of crude oil [16]. Previous work relating to the current project also showed the prospects of carbon-based nanoadditives to suppress microexplosion [20]. So, the prospects of mix additives made of polymer and carbon-based nanoadditive need to be explored for suppressing microexplosion, increasing ignition delay, and decreasing combustion rate of crudes leading to better crude oil fire safety. In addition, combustion behaviors of different emulsified fuels based on Jet-A (base fuel), water and ethanol were investigated.

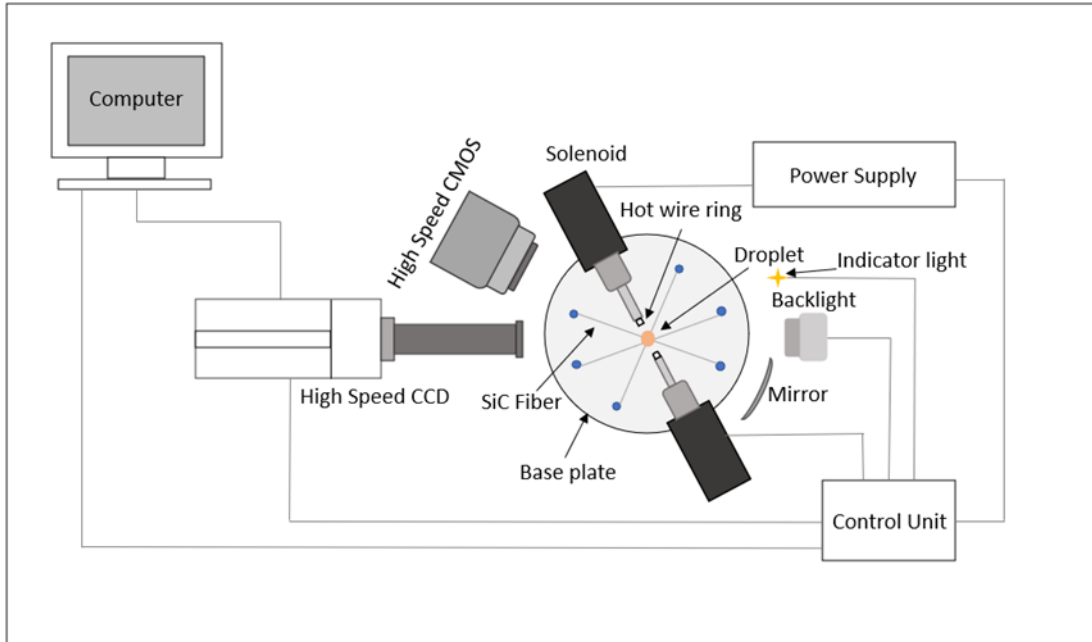
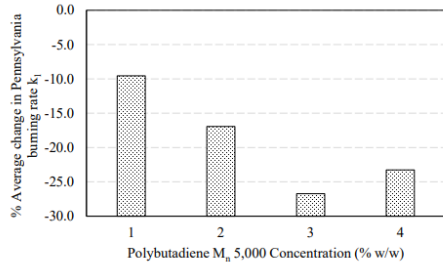


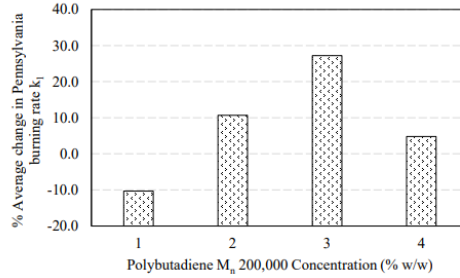
Figure 2.1 A Schematic diagram of the experimental apparatus to study the combustion of single droplet [19].

The conclusions are summarized as follows:

- A decrease in combustion rate is seen for Pennsylvania crude when PBD5k is added, with the largest decrease of 26% occurring at 3%w/w PBD5k (Figure 2.2a). PBD200k generally increases the combustion rate in Pennsylvania crude, with a maximum increase of 27% noted at 3%w/w (Figure 2.2a). A general decrease in combustion rate is noted for Bakken crude when PBD5k is added, with the largest decrease of 12% occurring at 2% w/w (Figure 2.3a). PBD200k is noted to generally increase combustion rate in Bakken crude, with the largest increase of 140% noted at 3%w/w (Figure 2.3b).

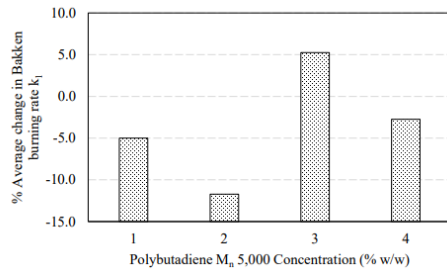


a)

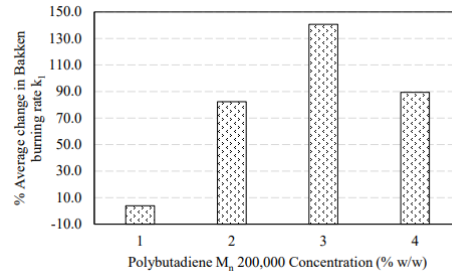


b)

Figure 2.2 Effect of (a) 5k and (b) 200k chain length PBD on Pennsylvania crude oil average combustion rate k_1 [16].



a)



b)

Figure 2.3 Effect of (a) 5k and (b) 200k chain length PBD on Bakken crude oil average combustion rate k_1 [16].

- Both PBD5k and PBD200k can be expected to decrease vapor pressure and inhibit diffusion of lighter components to the surface to decrease combustion rate, but faster thermal degradation and increased thermal conductivity of PBD200k result in an overall increase in combustion rate, thereby making PBD5k a much more likely additive for crude oil transportation safety.
- A decrease in ignition delay is noted for Pennsylvania crude when PBD5k is added, with the largest decrease of 26% occurring at 1% w/w (Figure 2.4a). Generally, addition of PBD200k to Pennsylvania crude causes an increase in

ignition delay, with the largest increases of 6% occurring at 1% and 3% w/w (Figure 2.4b). This can be explained by a larger ignition delay associated with PBD200k because of its larger chain length.

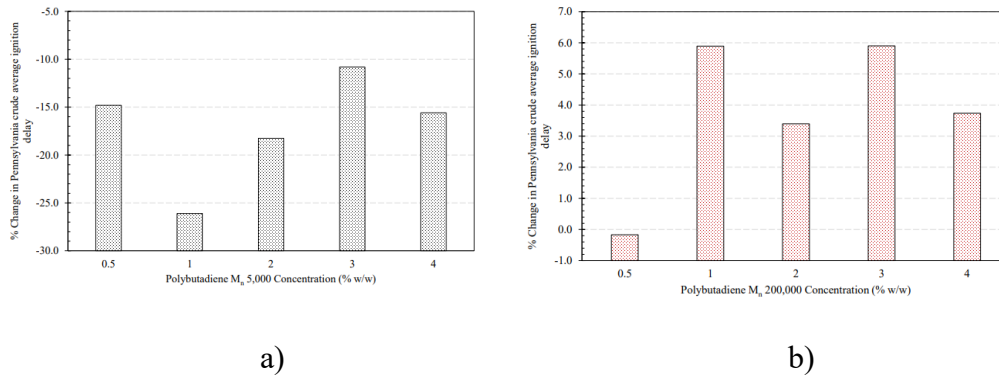


Figure 2.4 Effect of (a) 5k and (b) 200k chain length PBD on average ignition delay of Pennsylvania crude [16].

- A large increase in ignition delay for Bakken crude is noted on addition of both PBD5k and PBD200k. A maximum of 52% increase in ignition delay is observed for Bakken crude at an addition of 1% PBD5k (Figure 2.5a). A maximum of 42% increase can be observed in ignition delay for Bakken crude at an addition of 4% PBD200k (Figure 2.5b). This can be explained by Bakken crude having a lower ignition delay compared to Pennsylvania crude, and the addition of both PBD5k and PBD200k resulting in an overall decrease in ignition delay because of decreased vapor pressure.

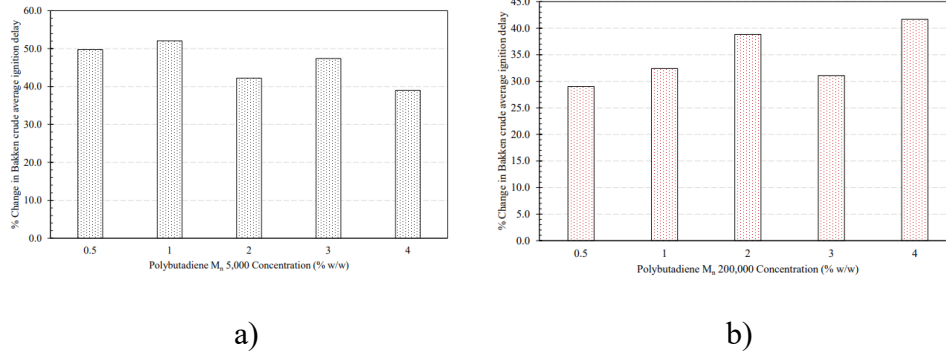
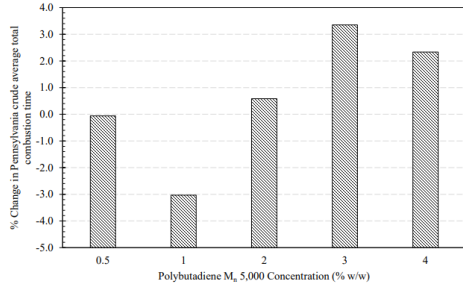
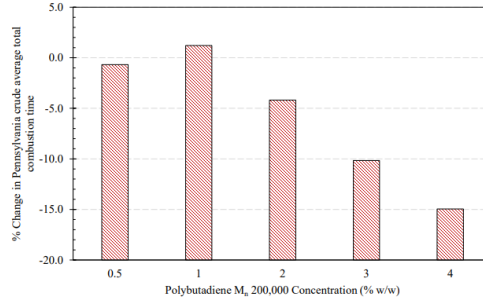


Figure 2.5 Effect of (a) 5k and (b) 200k chain length PBD on average ignition delay of Bakken crude [16].

- PBD5k causes a general increase in Pennsylvania crude total combustion time, with the greatest increase of 3.4% seen at 3% PBD5k (Figure 2.6a). This is caused by the decrease in combustion rate, as noted above. Addition of PBD200k generally causes total combustion to decline with the greatest average total combustion time decrease of 15% seen at 4% PBD200k (Figure 2.6b). This is caused by high intensity microexplosions at high PBD200k concentrations, which cause loss of liquid fuel. PBD5k causes a general decrease in Bakken crude total combustion time, with the greatest decrease of 8% seen at 3% PBD5k (Figure 2.7a). Adding PBD200k to Bakken crude greatly decreases total combustion time with the largest average total combustion time decrease of 28% noted at 4% PBD200k (Figure 2.7b). This can be explained by increased microexplosion intensity in Bakken crude when both PBD5k and PBD200k are added.

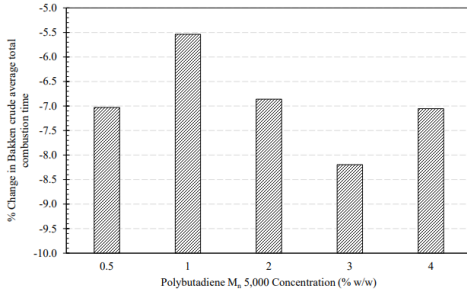


a)

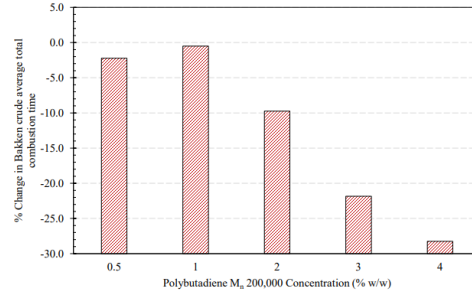


b)

Figure 2.6 Effect of (a) 5k and (b) 200k chain length PBD on average total combustion time of Pennsylvania crude [16].



a)



b)

Figure 2.7 Effect of (a) 5k and (b) 200k chain length PBD on average total combustion time of Bakken crude [16].

- Generally, a decrease in flame stand-off ratio (FSR) is noted when PBD5k is added to Pennsylvania crude. This is explained by the decrease in vapor pressure of crude oil with the addition of polymer, as noted above.
- SEM imaging of the soot deposits revealed that PBD5k-Bakken blends leave behind a more densely packed structure compared to pure Bakken (Figure 2.8). Individual average soot particle for PBD5k-Bakken blends was found to decrease to $\sim 40\mu\text{m}$ from $\sim 70\mu\text{m}$ in case of pure Bakken crude. Additionally, imaging of

the soot structure surface revealed globular polymeric structure embedded in the soot residue. Ultimately, soot structure of combustion residue is determined by the chemical make-up of the fuel.

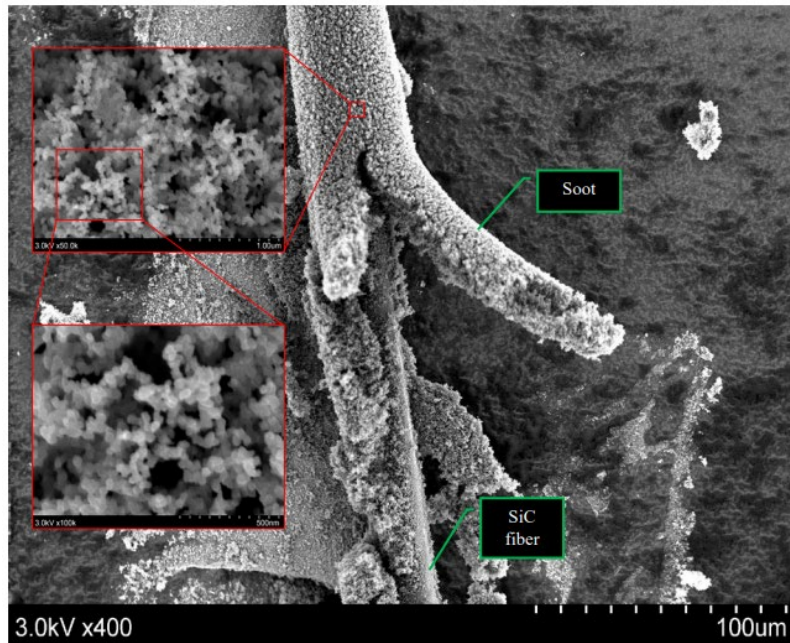


Figure 2.8 SEM images of 1% PBD5k-Bakken blend soot residue, showing soot structure at various levels of magnification. Individual soot particles can be seen [16].

- Nanofuel based on Jet-A with Carbon dots (CD) has four distinct combustion regimes while the pure Jet-A shows three combustion regimes (Figure 2.9). CD addition generally increase the combustion rate compared to base fuel (Figure 2.10a). On the other hand, CD addition generally decreases the ignition delay (Figure 2.10b) and Total combustion time compared to base fuel.
- Puffing is observed in both pure Jet-A fuel and nanofuels (Figure 2.11). With the addition of CD, an increase in puffing intensity is observed. Also, no distortion in flame structure is observed for pure Jet-A fuel droplets while distortion in flame

structure is observed for nanofuels (Figure 2.12). This is due to ejection of mass at higher speed due to higher intensity puffing. Puffing distorted the fuel droplet in the opposite direction of mass ejection while the flame structure is distorted in the same direction of puffing.

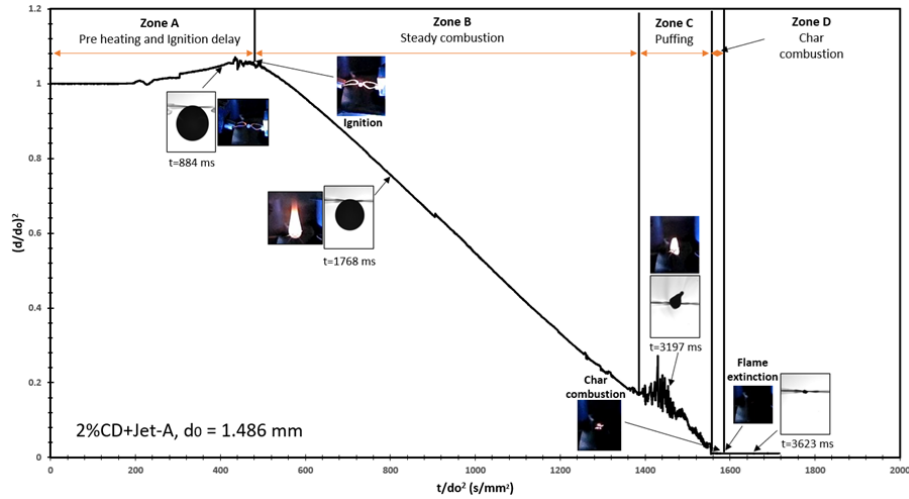


Figure 2.9 Different combustion regimes as observed in one of the five droplet experiments of 2% (w/w) CD with Jet-A fuel, $d_0=1.486$ mm [19].

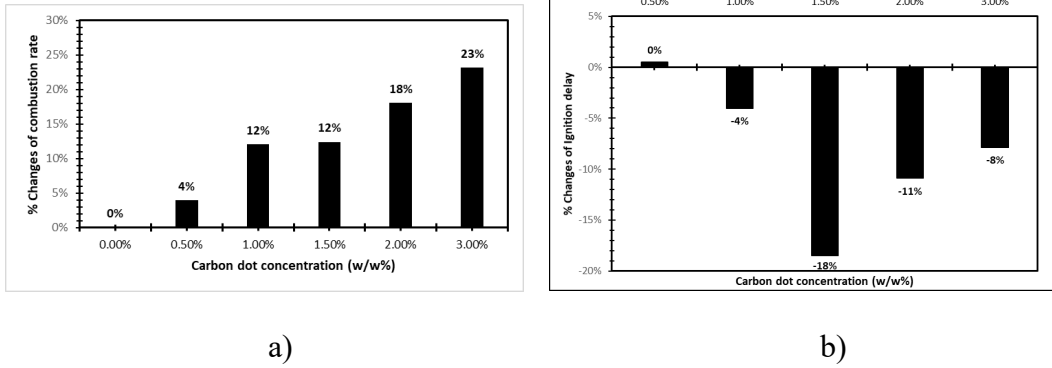


Figure 2.10 Percent changes in a) Combustion rate, and b) ignition delay of nanofuels compared to pure Jet-A [19].

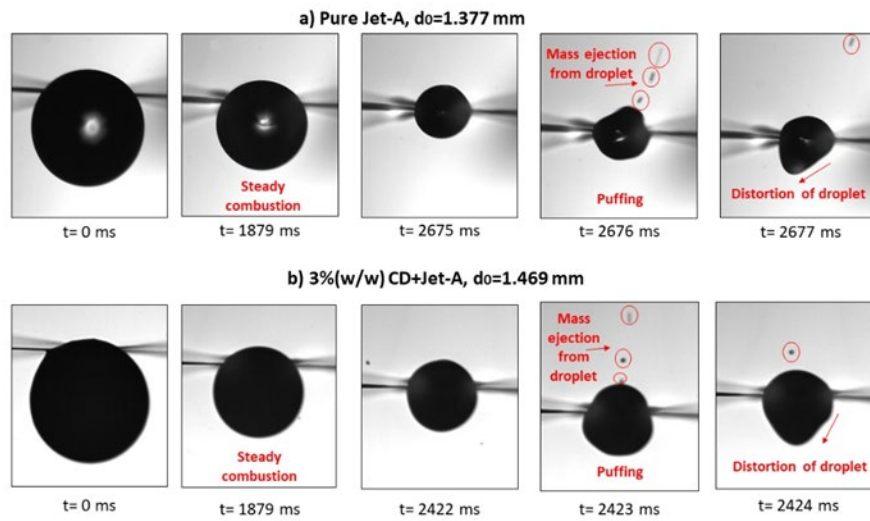


Figure 2.11 Puffing in a) Pure Jet-A fuel droplet, and b) 3%(w/w) CDs + Jet-A nanofuel droplet. Here $t=0$ ms defines as start of the experiment [19].

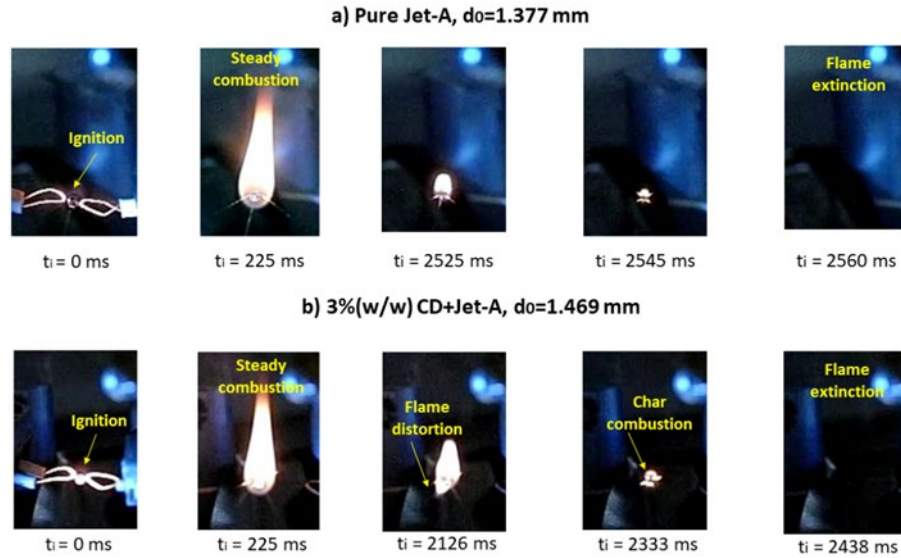


Figure 2.12 Flame propagation a) Pure Jet-A fuel droplet, and b) 3%(w/w) CD + Jet-A nanofuel droplet [19]. Here $t_i=0$ ms defines as start of the ignition.

- All the tested emulsified fuel showed a general trend following the d^2 -law of combustion (Figure 2.13). Also emulsified fuel showed puffing and microexplosion phenomena. Compare to base fuel (Jet-A), both types of emulsion (Jet-A-Water and Jet-A-Water-ethanol) showed a general decrease in combustion rate and droplet burning time but an increase in ignition delay. With the increase in water mass concentration, the decrease in combustion rate and droplet burning time is higher compared to lower water mass containing emulsions, and base fuel. Also, the ignition delay is higher for higher water mass containing emulsions.

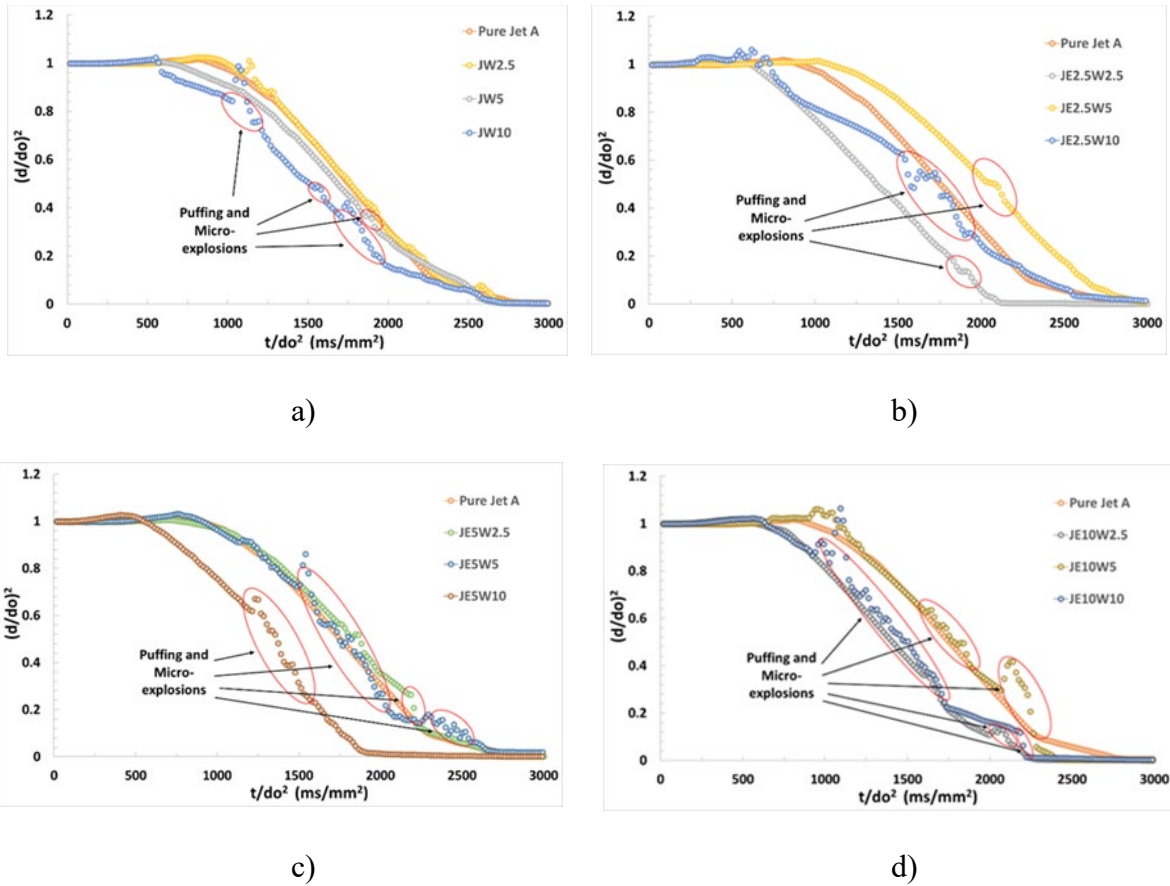


Figure 2.13 Normalized droplet diameter square evolution for a) Pure Jet-A and Jet-A–Water emulsified fuels; b-d) Pure Jet-A and ethanol-blended Jet-A–Water emulsified fuels droplets [17].

These results will aid in further investigation to unravel the inherent mechanisms for obtaining a prolonged stability period for surrogates and crudes with additives (nanoadditives and polymers) and the prospects of polymer/nanoadditive blends and their optimum concentrations to enhance fire safety of crude oil during shipping by rail.

2.2 Settling Characterization

Polymeric additives can be used to modify different surrogate properties like viscosity, surface tension, and burning rates. The stability of such surrogate-polymer suspensions over time is an object of investigation.

Manual tests as well as experiments with the inhouse stability period experiment setup (Figure 2.14) have been utilized to study the settling characteristics of carbon-based nanofuel, and emulsified fuel. In practical application, fuel need to be stored for a prolonged period for their operation and use. From the last three years' findings, it can be concluded that the settling experiment setup can quantitatively measure the settling and stability period [21][22][23][24]. This settling experiment setup will be exploited to investigate how the settling/stability period can be improved (with the application of surfactants or functionalized characteristics of nanoadditives) for surrogates with carbon-based nanoadditives and polymers. Stability period of Jet-A based emulsified fuel data were generated using the stability experiment setup (Figure 2.16 through 2.17). Also, the settling period of nanofuel based on carbon dot and surrogates were explored (Figure 2.15).

These data were presented at a conference and formed into a conference paper. Also, two other manuscripts are under development. This data is expected to help in exploring the basic physics behind the settling of real-world nanofuels and nanofluids, which will further help in developing nanoadditives for realistic crude oils and their surrogates.

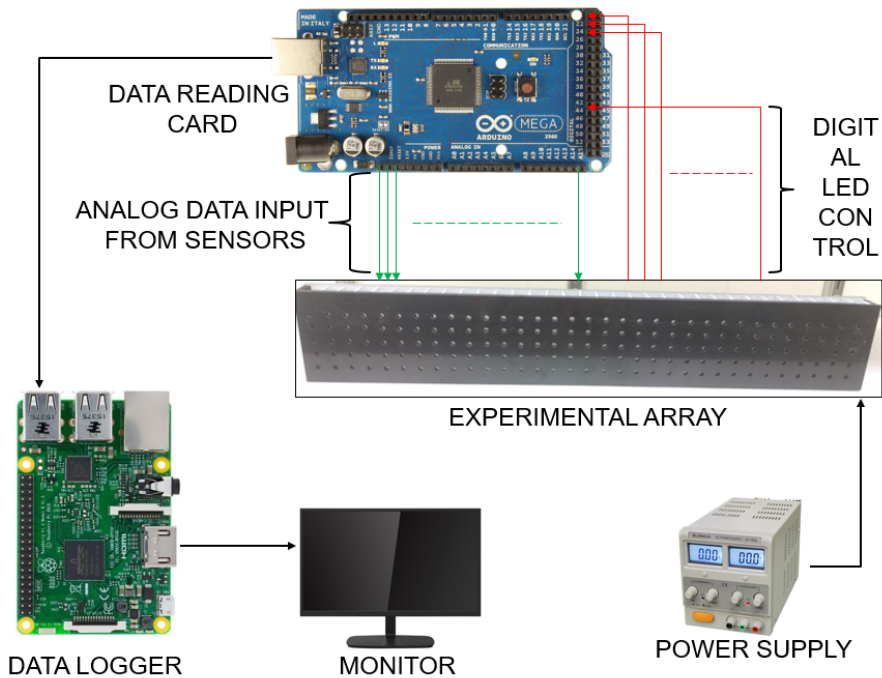


Figure 2.14 Main components of settling analysis experiment.

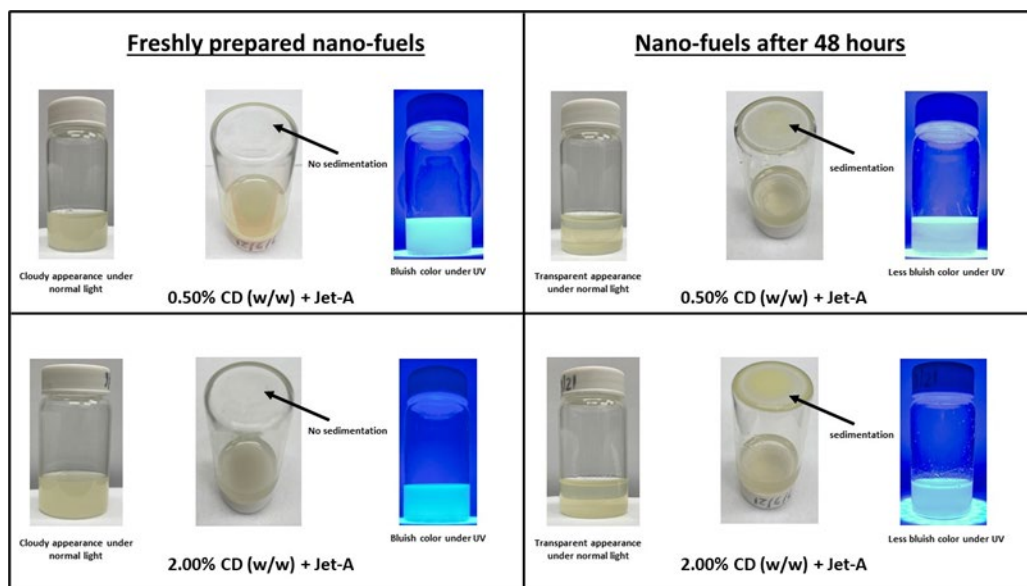


Figure 2.15 Images of freshly prepared nano-fuels and nano-fuels after 48 hours of preparation. Top images are for 0.50% CD (w/w) + Jet-A nano-fuel and bottom images are for 2.00% CD (w/w) + Jet-A nano-fuel [19].

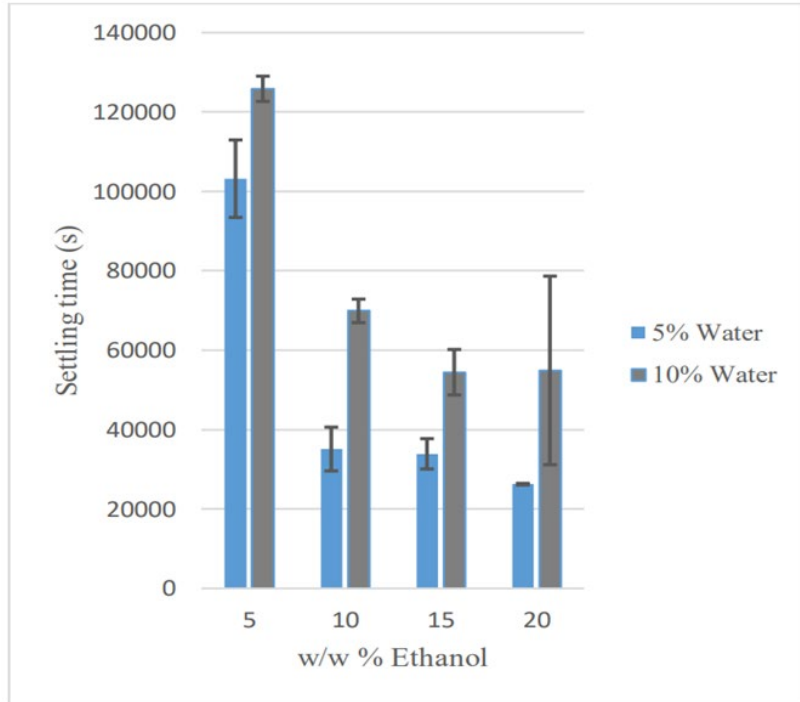


Figure 2.16 Graphical representation of observed settling times in seconds for different Jet-A based emulsified fuels [18].



Figure 2.17 Emulsified fuel (10E5W) sample immediately a) after ultrasonication, and b) after phase separation [18].

Chapter 3 Collaboration and Publications

3.1 Collaboration

The hardware for the settling has been constructed and is generating data. One of the settling arrays, along with its data acquisition and logging system, is being used by a visiting scholar. He reports to Prof. Daniela Becker at Center of Technological Sciences, Santa Catarina State University, Joinville, Santa Catarina, Brazil.

Assistant Professor Mehdi Esmaeilpour (Marshall University, Marshalltown, WV, USA) is involved in post-processing of data as well as preparation of technical manuscripts.

Professor Dr. Roger M. Leblanc's group from the University of Miami (Coral, Gables, FL, USA) synthesized the gel like carbon dots.

3.2 Publications

All papers and posters listed here have been possible because of the work undertaken through December 31, 2021.

Research papers:

- Singh, G., Esmaeilpour, M., & Ratner, A. (2021). Effect of polymeric additives on ignition, combustion and flame characteristics and soot deposits of crude oil droplets. *Combustion Science and Technology*, 1-29.

Conference papers:

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